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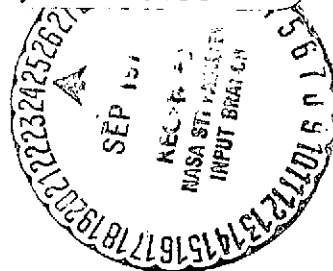
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16. Abstract

An evaluation of the thermodynamic characteristics of the hydration and dissociation of HO$_2$ is presented.

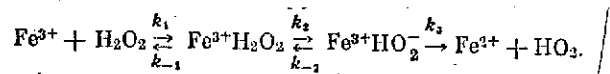| 17. Key Words (Selected by Author(s))	18. Distribution Statement Unlimited		
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The thermodynamic characteristics of the hydration and /2658* dissociation of HO$_2$ were determined.

It was shown in [1] that the formation of radicals in the system Fe^{3+} + H$_2$O$_2$ occurs by the mechanism

$$Fe^{3+} + H_2O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Fe^{3+}H_2O_2 \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} Fe^{3+}HO_2^- \overset{k_3}{\rightarrow} Fe^{2+} + HO_2.$$

Moreover the first two phases can be calculated by the equilibria /2659

$$k_{eff} = \frac{k_1}{k_{-1}} \cdot \frac{k_2}{k_{-2}} k_3.$$

The rate constant $k_{eff} = 2.10^{-5} sec^{-1}$ at 25°C and at neutral ionic strength. In [2] it was found that the rate constant of the reaction Fe^{2+} + HO$_2$ is equal to $2.1.10^6$/mol·sec at 25°C and does not depend on the acidity of the medium, and the initial product of the reaction is the complex Fe^{3+} + HO$_2^-$. This indicates that the limiting phase here is the replacement of water in the coordination shell of the Fe^{2+} ion. Thus the ratio can be written

$$K_e = \frac{k_1}{k_{-1}} \cdot \frac{k_2}{k_{-2}} \cdot \frac{k_3}{k_{-3}} = \frac{k_{eff}'}{k_{-3}} = e^{-\Delta z_0 / RT}$$

where K_p is the equilibrium constant of the reaction

$$Fe^{3+} + H_2O_2 \rightleftarrows Fe^{2+} + HO_2.$$

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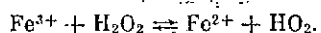
*Numbers in the margin indicate pagination in the foreign text.

We find $K_p = 9.5 \cdot 10^{-12}$ and $\Delta Z_0 = 15.1$ kcal.

Knowing the standard redox potential of Fe^{3+}/Fe^{2+} (0.771 in [3]), we find the standard free energy $\Delta Z_0 = -32.9$ kcal for the reaction
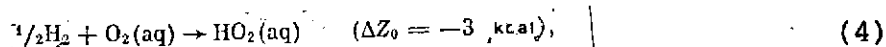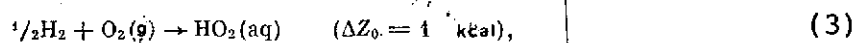
$$\tfrac{1}{2}H_2 + HO_2(aq) \rightarrow H_2O_2(aq). \qquad (1)$$

Since $\Delta Z_0 =$ (diss. H_2O_2) $= 15.9$ kcal [4], for the reaction

$$\tfrac{1}{2}H_2 + HO_2(aq) \rightarrow HO_2^- + H^+ \qquad (2)$$

we obtain $\Delta Z_0 = -17$ kcal. The most probable values of the standard free energy of formation and hydration of H_2O_2 are equal to -25.2 and -6.7 kcal [4, 5] respectively.
From this we get

$$\tfrac{1}{2}H_2 + O_2(g) \rightarrow HO_2(aq) \qquad (\Delta Z_0 = 1 \text{ kcal}), \qquad (3)$$

$$\tfrac{1}{2}H_2 + O_2(aq) \rightarrow HO_2(aq) \qquad (\Delta Z_0 = -3 \text{ kcal}), \qquad (4)$$

since $\Delta Z_{\text{hydrO}_2} = 4$ kcal [6]. Using known values for the standard entropies of H_2, HO_2 and H_2O_2 (31.2; 55.17, and 55.66 E.U. respectively [7]), the entropies of hydration of HO_2 and H_2O_2 (-22 and -24.8 E.U. [4,8,9]) and the entropy of acid dissociation of H_2O_2 (-25.8 E.U. [4]), we find the ΔH_0 and ΔS_0 for reactions (1) and (2).
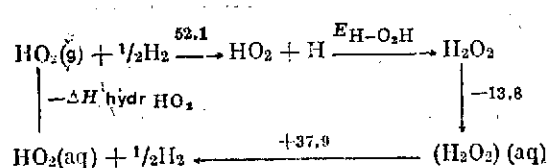
We now calculate the ΔS_0 for the acid dissociation of HO_2. From the entropic cycle

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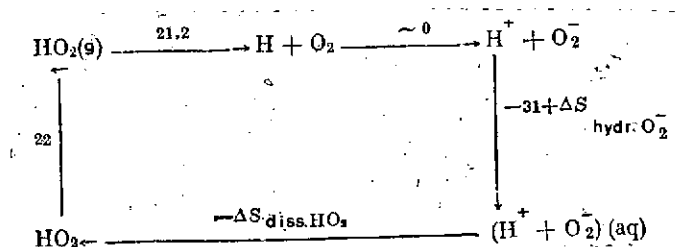
we find $\Delta S_{hydrO_2^-} - \Delta S_{dissHO_2} = -12.2$ E.U. The entropies of hydration of polyatomic ions monatomically increase in proportion to the decrease of the radius of the ion in solution [10, 11]:

ANION	OH^-	CN^-	NO_3^-	ClO_4^-
ΔS_{hydr}	-40.6	-19.9	-19.5	-16.3
Radius of ion in solution $\overset{o}{A}$	1.53	1.89	1.92	2.36

It is reasonable to assume that the radius of the O_2^- ion-radical in solution is intermediate between the radii of CN^- and NO_3^-. This indicates that the most probably value for the entropy of hydration of O_2^- is equal to the mean value (-19.7 E.U.) of the entropies of hydration for these anions. We then obtain -7.5 E.U. for the most probable value of ΔS_{dissHO_2}. The free energy of dissociation of HO_2 is equal to 6.65 kcal ($p^K_{HO_2}=$ 4.88 [11]). For the enthalpy of dissociation we get $\Delta H= 4.4$ kcal. As a result we find the values for standard entropies and enthalpies of reactions (5) and (6) (see the Table). With the aid of the cycle
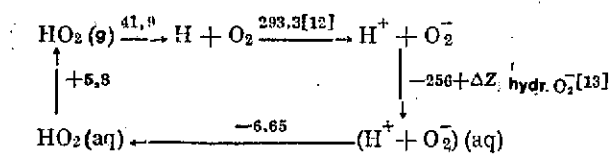
$$HO_2(g) + \tfrac{1}{2}H_2 \xrightarrow{52.1} HO_2 + H \xrightarrow{E_{H-O_2H}} H_2O_2$$
$$\downarrow{-\Delta H_{hydr\,HO_2}} \qquad\qquad\qquad \downarrow{-13.8}$$
$$HO_2(aq) + \tfrac{1}{2}H_2 \xleftarrow{+37.9} (H_2O_2)(aq)$$

we find $E_{H-O_2H} - H_{hydrHO_2} = 76.3$ kcal.

Number	Reaction	ΔH_0, kcal	ΔS_0, E. U.	ΔZ_0, kcal	E_0, V
1	$\tfrac{1}{2}H_2 + HO_2(aq) \longrightarrow H_2O_2(aq)$	—37,9	—16,9	—32,9	1,43
2	$\tfrac{1}{2}H_2 + HO_2(aq) \longrightarrow HO_2^- + H^+$	—29,7	—42,7	—17,0	0,74
3	$\tfrac{1}{2}H_2 + O_2(g) \longrightarrow HO_2(aq)$	—8,4	—31,4	1,0	—0,04
4	$\tfrac{1}{2}H_2 + O_2(aq) \longrightarrow HO_2(aq)$	—5,4	—8,2	—3,0	0,13
5	$\tfrac{1}{2}H_2 + O_2(g) \longrightarrow O_2^- + H^+$	—4,0	—38,9	7,7	—0,33
6	$\tfrac{1}{2}H_2 + O_2(aq) \longrightarrow O_2^- + H^+$	—1,0	—15,7	3,7	—0,16
7	$HO_2(g) \longrightarrow HO_2(aq)$	—12,4	—22,0	—5,8	—
8	$O_2^-(g) \longrightarrow O_2^-(aq)$	—84,0	—19,7	—78,0	—
9	$HO_2 \longrightarrow H^+ + O_2^-$	—4,4	—7,5	6,65	—

Assuming E_H-O_2H = 88.6 kcal [12], we get ΔH_{hydrHO_2} = -12.4 kcal. According to [12] the energy error for the breaking of OH bonds in peroxide amounts to ± 2 kcal. But if E_{H-O_2H} is in fact equal to 90.6 kcal, then for ΔH_{hydrHO_2} we would get 14.3 kcal. This is why a greater heat of hydration for peroxide is not very likely. When E_{H-O_2H} = 86.6 kcal, the value becomes $H_{hydr}HO_2$ = 10.3 kcal, which is approximately equal to the heat of evaporation of water and also scarcely probable. The most reasonable hypothesis is that the heat of hydration of HO_2 falls between the heat of evaporation of water and the heat of hydration of peroxide. The value we found meets this condition. Obviously, E_{H-O_2H} = 86.6 kcal is more exact, but the error for the values of E_{H-O_2H} and ΔH_{hydrHO_2} did not exceed 1 kcal. Using ΔS_{hydrHO_2} = -22 E.U. we find that ΔZ_{hydrHO_2} = - 5.8 kcal. By means of the cycle

$$HO_2(g) \xrightarrow{41.9} H + O_2 \xrightarrow{293.3[12]} H^+ + O_2^-$$

$$\uparrow +5.8 \qquad\qquad \downarrow -256 + \Delta Z_{hydr.\ O_2^-}[13]$$

$$HO_2(aq) \xleftarrow{\qquad -6.65 \qquad} (H^+ + O_2^-)(aq)$$

it is possible to obtain a sufficiently accurate value for the free energy of hydration of O_2^-, which is equal to -78 kcal, from which we find $\Delta H_{hydrO_2^-}$ = -84 kcal.

As the next procedure, we conducted additional verification of the values found. According to [14], the ratio $(k_{Fe^{3+}} +O_2^- k_{dissHO_2})/k_{Fe^{2+}}$ = HO_2 = $7 \cdot 10^{-3}$ mol/1 at 25°C, and the energy of activation for this ratio is equal to 1.2-4 kcal. We have $k_{Fe^{3+}} +O_2$ = $1.1 \cdot 10^9$/mol·sec. ,Since the limiting phase of the reaction $Fe^{2+} +HO_2$ is the replacement of water in the hydrated shell of the Fe^{2+} ion, the energy of activation $E_{Fe^{2+}} +HO_2$ must be close to the energy of activation for replacement, i.e., 8.3 kcal [15]. Using ΔH_{dissHO_2} = 4.4 kcal, we arrive at the result

$E_{Fe^{3+} O_2^-} = 5.1-7.9$ kcal. Assuming $E_{Fe^{3+} O_2^-}$ to be $= 6.5$ kcal, we obtain $k_{Fe^{3+} O_2^-} = 10^{14}e^{-6500RT}$. However, taking account of a considerable positive input into the energy of activation, which corresponds to the reaction between inversely charged molecules (in the given case from three to six orders of pre-exponential magnitude), we must recognize the value found of the energy of activation as completely reasonable   In [8] the value $\Delta S_{dissHO2} = -27$ E.U. was used, giving $\Delta H_{dissHO_2} = -1.4$ kcal and $E_{Fe^{3+} + O_2^-} = 10.9 - 13.7$ kcal, which signifies an abnormally high value for the pre-exponential factor and is, obviously, unreliable.

According to [16], the rate constant for the reaction $Cu^{2+} = O_2^-$ is equal to 2.10^9 1/mol.sec at 25°C. According to our data, we find $\Delta H = 2.7$ kcal for this reaction, which allows a possibility of a low energy of activation for it. For example, if the energy of activation of the reverse reaction is ~ 2 kcal, then, for the reaction under consideration, we obtain $E_{act} \sim 5$ kcal, which gives $k_{Cu^{2+} + O_2^-} = 10^{13}e^{-5000/RT}$. Because of reasons analogous to that shown above for the reaction $Fe^{3+} + O_2-$, the value of the pre-exponential factor is also reliable here. But if the data in [8] is used, then for this reaction we obtain $\Delta H = 8.5$ kcal and $E_{act} \sim 10.5$ kcal, which, obviously, is not very likely for so rapid a reaction. The results of the calculation of the thermodynamic characteristics of HO_2 in an aqueous solution are presented in the table. The error for the values of E_O, which correspond to reactions (1) - (6), apparently does not exceed 0.01 V. The error for the values of ΔH_O and ΔS_O, evidently, does not exceed 1 kcal and 3-4 E.U., respectively. Approximately, then, this is the accuracy of the values corresponding to reactions (7) - (9).

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REFRENCES

1. V.M. Berdnikov, O.S. Zhusavleva, Kinetika i Kataliz (Kinetics and Catalysis), in press.

2. G.G. Jayson, J.P. Keene, D.A. Stirling, A.J. Swallow, Trans, Faraday Soc., 65, 2454, 1969.

3. Yu.Yu. Lur'ye, Spravochnik po Analiticheskoy Khimii (Reference source on Analytic Chemistry), "Khimiya" Press, Moscow, 1967.

4. U. Shamb, Ch. Setterfield, R. Ventuors, Perehis' Vodoroda (Hydrogen Peroxide), Foreign Lit. Press, Moscow, 1958.

5. M.Kh. Karapet'yants, M.L. Karapet'yants, Osnovnyye Termodinamicheskie Konstanty Neorganicheskikh i organicheskikh Beshchest v (Basic Thermodynamic Constants of Inorganic and Organic Substances), "Khimiya" Press, Moscow, 1968.

6. R.A. Pierotti, J. Phys. Chem., 69, 281, 1965.

7. A.V. Gurvich, Termodinamicheskiye svoystva individual'nykh veshchestv T. I, (Thermodynamic properties of individual substances, Vol. I.) AN SSSR Press, Moscow, 1962.

8. Yu.I. Skurlatoo, Zh. Fiz. Khimii (Journal of Physical Chemistry), 44, 548, 1970.

9. V.M. Berdnikov, N.M. Bazhin, Zh. Fiz. Khimii ([as above]), 44, 712, 1970.

10. Kratkiy spravochnik fiziko-ximicheskikh velichin (Short listing of Physical-Chemical Constants), "Khimiya" Press, Moscow, 1967.

11. D. Behar, D.B.J. Czapski, J. Rabani, L.M. Dorfman, H.A. Schwarz, J. Phys. Chem., 74, 3209, 1970.

12. V.I. Vedeneyev, Energiya razryva svyazey (Energy of the Breaking of Bonds), Moscow, 1962.

13. V.E. Conway, J.O.M. Bockris, in the collection
    Nekotoryye problemy sovremennoy elektrokhimii
    (Some Problems of Modern Electrochemistry), Foreign
    Literature Press, Moscow, 1958.

14. W.O. Barb, J.H. Bakendale, P. George, K.R. Hargrave,
    Trans. Faraday Soc., 47, 464, 1951.

15. N. Sutin, Ann. Rev. Phys. Chem., 17, 119, 1966.

16. Yu.N. Kozlor, V.M. Berdnikov, Zh. Fiz. Khimii
    (Journal of Physical Chemistry), in press.